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The status of natural gas hydrate research in China: A review

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ABSTRACT

Over the past century, fossil fuels have provided the majority of China's energy. However, their extensive utilization leads to a shortage and environmental pollution. Recently, submarine and permafrost gas hydrate deposits have been investigated as a possible clean and sustainable energy source by governmental institutions, research organizations, and energy industries in China. The primary objective of this paper is to review the potential studies pertaining to gas hydrate exploration and resource assessment, the safe and efficient exploitation of gas hydrates and the basic properties of gas hydrates. To date, there are over 20 institutions and organizations in China committed to gas hydrate investigation, among which the Guangzhou Marine Geological Survey (GMGS) and the Chinese Academy of Geological Sciences (CAGS) etc. primarily focus on gas hydrate exploration research, while the China National Offshore Oil Corporation (CNOOC) Research Center, Guangzhou Institute of Energy Conversion (GIEC) and China University of Petroleum-Beijing (CUPB) etc. concentrate on gas hydrate mining technologies. In this paper, the occurrence and exploration of gas hydrates in both permafrost regions and the continental slope of China have been determined from numerous research contributions and are presented. Moreover, the latest progress in gas hydrate fundamental studies, including hydrate phase equilibria, hydrate formation mechanisms, hydrate thermal physical properties and the acoustics and resistivity characteristics of gas hydrates are briefly reviewed, and relevant data are gathered and compared. Emphasis is also placed on gas hydrate mining technologies and gas production using depressurization methods, thermal stimulation methods or other methods. Furthermore, the security of natural gas hydrate-bearing sediments during gas production and the environmental impacts of gas hydrate are identified. With additional financial and political support and advanced research facilities, research on gas hydrates in China is progressing rapidly but is still in its early developing stage, thus, future work should be undertaken with greater diligence.

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1. Introduction

Fossil fuels currently satisfy approximately 85% of the world's commercial energy needs [1]. Considering that conventional fossil fuel resources are being exhausted and the continuously increasing energy demand, locating a sustainable alternate energy source is essential and urgent. Gas hydrates, which exhibit high energy density, are clean, and for which a large amount of resources are available, are generally accepted as a potential strategic energy form for sustainable development [2]. Over the last decade, there has been a tremendous increase in gas hydrate studies, and more capital has been invested and more governmental agencies are becoming involved in this popular field.

Gas hydrates are ice-like solid crystalline compounds formed by small gas molecules, such as methane, with cages of water framework called hosts [3]. To date, three types of gas hydrate structures have been studied: structure I, structure II and structure H. Gas hydrates are formed under suitable conditions of low temperature and high pressure, which implies that gas hydrates are found in two different geographic settings: the permafrost and the continental slope. One of the most important reasons why gas hydrates attract the world's attention is that 1 m^3 of gas hydrate may contain as much as 180 m^3 of gas at standard temperature and pressure, and the amount of carbon in hydrate form is twice the total carbon amount in fossil fuel form on the earth [4]. Gas hydrates were first discovered in laboratory studies in 1810; however, no further attention was paid to these materials until the 1930s, when petroleum engineers observed that hydrates contributed to the plugging problem of natural gas transport pipelines [5]. In the past four decades, with the gradual discovery of large amounts of natural gas hydrate sediments and a better understanding of the properties of gas hydrates, researchers have increasingly devoted themselves to the study of gas hydrates, more scientific achievements have been contributed and more high-quality papers have been published. Meanwhile, new technology based on hydrate studies are being developed, including gas separation [6], gas storage and transportation [7–9] and CO_2 sequestration [10].

In China, research on nature gas hydrate began in the 1990s when a research group at the China University of Petroleum-Beijing (CUPB) initiated fundamental studies on gas hydrates [11]. Hydrate phase equilibria and the kinetics of hydrate formation and dissociation were first studied in 1995 at the High Pressure Fluid Phase Behavior and Property Research Laboratory of CUPB [5]. In the mid-1990s, the Guangzhou Institute of Energy Conversion (GIEC) of the Chinese Academy of Sciences (CAS) began studies on the hydrate-based thermal energy storage technique. Currently, there are more than 20 research groups in China working in various fields of hydrate investigation, especially in studies on gas hydrate exploration and exploitation. Among these research organizations, GMGS, the Institute of Mineral Resources (IMR) of CAGS, the Ocean University of China (OUC) and the Institute of Oceanology, Chinese Academy of Sciences (IOCAS) etc. mainly focus on gas hydrate exploration studies, and studies on gas hydrate exploitation technologies are chiefly conducted by the CNOOC Research Center, GIEC and CUPB etc. In addition, Dalian University of Technology (DUT), Zhejiang University (ZJU), China University of Geosciences (CUG), Guangzhou Institute of Geochemistry (GIG), the Institute of Geology and Geophysics (IGG) and Qingdao Institute of Marine Geology (QIMG) etc. also play a significant role in gas hydrate investigation. Meanwhile, many research projects have been subsidized by government departments, including the National High Technology Research and Development Program (863), the National Key Basic Research and Development Program (973), National Science and Technology Major Projects, and the National Natural Science Foundation.

In this study, the latest progress in gas hydrate-related research in China is briefly reviewed, including the exploration of natural gas hydrate, basic property research, exploitation technology and the security of nature gas hydrate exploitation.

2. Natural gas hydrate exploration in China

Natural gas hydrates are widely distributed in permafrost regions and the continental slope, where the temperature and pressure conditions are suitable for formation. It is estimated that the global amount of hydrate-bound gas is approximately 2.5×10^{15} m^3 for methane [12]. More than 230 natural gas hydrate deposits (NGHD) have been discovered worldwide in 79 countries [3]. Recently, the exploration of natural gas hydrates has been active around the world in seafloor areas and permafrost regions.

In China, natural gas hydrates exist abundantly in both permafrost and seafloor areas. In the Qinghai–Tibet plateau permafrost area, geological, geophysical and geochemical studies have indicated the presence of gas hydrates. Samples of gas hydrates were collected in Qilian Mountain permafrost during 2008–2009, representing the first discovery of gas hydrates in permafrost of China [13]. The amount of natural gas caged in hydrates in permafrost regions of the Qinghai–Tibet Plateau ranged from approximately 1.2×10^{11} to 2.4×10^{14} m^3 [14]. In addition, the existence of gas hydrates in the South China Sea (SCS) has been geologically, geophysically and geochemically confirmed. The preliminary results indicated that the estimated inventory of natural gas in the SCS was 6.5×10^{13} m^3, i.e., 65 billion tons of oil equivalent with a 50% confidence level [15].

2.1. Gas hydrate exploration in permafrost regions

The Qinghai–Tibet Plateau, located in southwestern China, extends for a maximum of 2945 km from east to west and for 1532 km across 13° of latitude. A considerable portion of the Qinghai–Tibet Plateau is underlain by permafrost with different thicknesses. The latest studies have indicated that the permafrost in the Qinghai–Tibet Plateau accounts for nearly 80% of the total permafrost area in China (2.15×10^6 km^2) [16]. The particular geographical and climatological conditions provide suitable temperature and pressure conditions for gas hydrate formation. In recent years, geological, geophysical, and geochemical investigations were conducted in the Qinghai–Tibet plateau permafrost, resulting in prospective gas hydrate occurrence areas, relevant resource assessment and sample collection [17–20].

Many institutes, including CAGS and GIG, are making substantial efforts in gas hydrate exploration in the Qinghai–Tibet Plateau permafrost regions, and scientists such as Youhai Zhu, Duofu Chen and Zhenquan Lu et al. have contributed to this work. There are various factors determining the potential occurrence of gas hydrate in permafrost areas, including the annual surface temperature, the geothermal gradient, the permafrost thickness and the pressure conditions.

Relevant data reveal that the mean annual surface temperature of the permafrost areas ranges from −0.2 to −4.0 °C and reaches lower than −5 °C in the extreme high mountains [21]. He et al. conducted a geologic survey, geochemical exploration, geophysical survey and drilling project in the Tuonamu area Qiangtang basin (Fig. 1) [22]. These researchers observed that even though the strong solar radiation is unfavorable for the preservation of the permafrost, the large amount of rainfall and the long duration of snow cover contribute to a low ground temperature. According to the measured data, there are three low temperature centers in the Qinghai–Tibet Plateau [23], and Qiangtang basin is mainly located in the largest one, where the mean annual ground temperature is lower than −6 °C, which is advantageous for the potential occurrence of gas hydrate.

The geothermal gradient and permafrost thickness are of great importance for the formation of gas hydrate. The analysis of ten borehole temperatures along the Qinghai–Tibet Highway indicated that the geothermal gradients within the permafrost ranged from 1.8 to 6.6 °C/100 m with an average of 4.6 °C/100 m [24]. The geothermal gradient is determined by numerous factors such as the soil and water features and the climate. The permafrost thickness is restricted by the thermal gradient, and these parameters affect each

Table 1
Characteristics of permafrost regions and gas hydrates [21,26].

Location	Permafrost thickness (m)	G_p [a] (°C/100 m)	G_t [b] (°C/100 m)	GHBS[c] (m)
Messoyakha 71°N, 86°E	320	0.6	1.8	500–1500
Alaska 69–71°N, 146–160°E	174–630	1.5–4.5	1.6–5.2	320–700
Mackenzie delta 69.5°N, 134–135°E	510–740	1.8	2.7	800–3000
Qinghai–Tibet Plateau 32–37°N, 92–95°E	> 130	1.1–8.0	2.5–8.5	Unknown

[a] Geothermal gradients within permafrost.
[b] Geothermal gradient beneath permafrost.
[c] Stability thickness of gas hydrate.

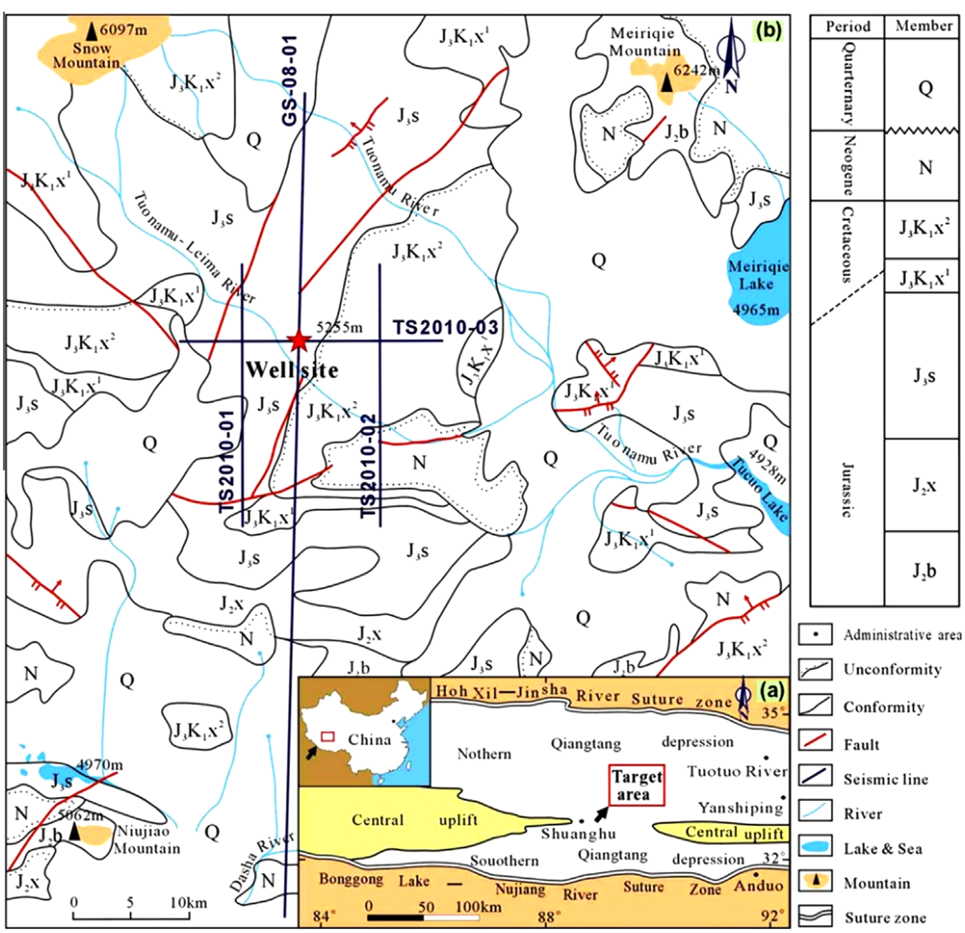


Fig. 1. (a) Simplified tectonic map of the Qiangtang basin identifying the location of the target area. (b) Simplified geological map of the Tuonamu area [22].

other. Recent drilling in the Qinghai–Tibet Plateau revealed that the permafrost thickness is greater than 128 m in the Wa-Li-Xi-Li-Tang Basin and as high as 139.4 m in Qilian Mountains [25]. Compared with permafrost in other areas around the world (Table 1) [21,26], the geothermal gradient and permafrost thickness of the permafrost in the Qinghai–Tibet Plateau are conducive for the possible formation of gas hydrate.

Temperature and pressure increase with depth underground, and there must be particular areas suitable for hydrate formation. Studies have demonstrated that gas hydrates can be stabilized at −13.2 to 12.9 °C and 1.0–50.0 MPa [22]. He et al. [22] calculated the pressure of the core samples collected from the well and concluded that the gas hydrate in the Tuonamu area of the Qiangtang basin was most likely in the form of gas-hydrate–water.

Recently, gas hydrate exploration and drilling work have been performed in permafrost regions in the Qilian Mountains. The continuous escape of hydrocarbon gases was observed inside the permafrost interval at hole 33 in the Muli coal field in 2004 [27]. Further simple gas sample analysis revealed that the hydrocarbon gases contain as much as 38.07–75.90% methane. Therefore, the temperature–pressure conditions of the permafrost regions are feasible for gas hydrate formation based on the gas composition, annual surface temperature, permafrost thickness and geothermal gradients of hole 33. The calculation also indicates that the hydrate stability zone most likely occurs in the 171–574 m interval with a thickness of 403 m.

Moreover, the Scientific Drilling Project of Gas Hydrate in Qilian Mountain permafrost was implemented by the China Geological Survey in 2008 and 2009, and four scientific experimental wells were drilled in Qinghai Province in the northeast Qinghai–Tibet plateau (Fig. 2) [28]. A large amount of gas was released when the gas hydrate bearing cores were extracted under air tight conditions, and Raman spectroscopy identified CH_4 as the primary hydrate-forming gas, with secondary components of C_2H_6, C_3H_8, and CO_2, confirming a structure II gas hydrate, which geologically and geochemically indicated the existence of natural gas hydrate in the target area. During the drilling project, gas hydrate samples were collected under the permafrost zone in the 133–396 m interval [29], representing the first discovery of a gas hydrate sample in the permafrost of China.

Additionally, gas hydrate formation conditions and indications of gas hydrate occurrence potential in Mohe permafrost in northernmost China were comprehensively analyzed by Zhao et al. [30]. The effect of conditions including the thickness of the permafrost and geothermal gradients, temperature–pressure conditions, source and quantity of hydrocarbon gases, trap and migration conditions on the formation of gas hydrate in Mohe permafrost were primarily illustrated.

2.2. Gas hydrate exploration in the SCS

The SCS is one of the largest marginal seas in the western Pacific Ocean and is located in the south of mainland China and Taiwan with an area of approximately 3.5×10^6 km^2. The northern SCS covers 17–23°N/110–120°E, with a water depth varying from 30 m in the northern shelf area to more than 4500 m in the south sea basin. The existence of gas hydrates in the northern SCS has been geologically, geophysically and geochemically confirmed, with the indicators including seismic data showing a well-developed BSR, methane-derived carbonate evidence, the higher methane concentration from headspace gas, and a thinner sulfate reduction zone. In particular, the geological factors play an important role in the formation of hydrates, including the tectonic constraint, submarine morphology and sediment facies, gas source, and temperature and pressure conditions for gas hydrate stability [31].

A Chinese–German coadjutant project was conducted in early 2004 with the aim of distributing methane and gas hydrates in the northern SCS. A 30-m high carbonate structure with bacterial patches and fissures in the east of Dongsha Islands was named Jiulong methane reef (Fig. 3) [32], which was the first direct evidence of methane seepage in the SCS. The reef is located on the northern continental slope with a water depth between 500 and 800 m and covers 430 km^2. Morphologically, there are three types of authigenic carbonates: chemoherm carbonates, seepage-associated concretions and gas hydrate-associated concretions. The carbonate samples collected by the TV-guided grabs were comparable to cold seep carbonates discovered worldwide. Based on the study of the samples, all the lithologically, mineralogically and geochemically characteristics indicated that the carbonates were derived from biogenic methane.

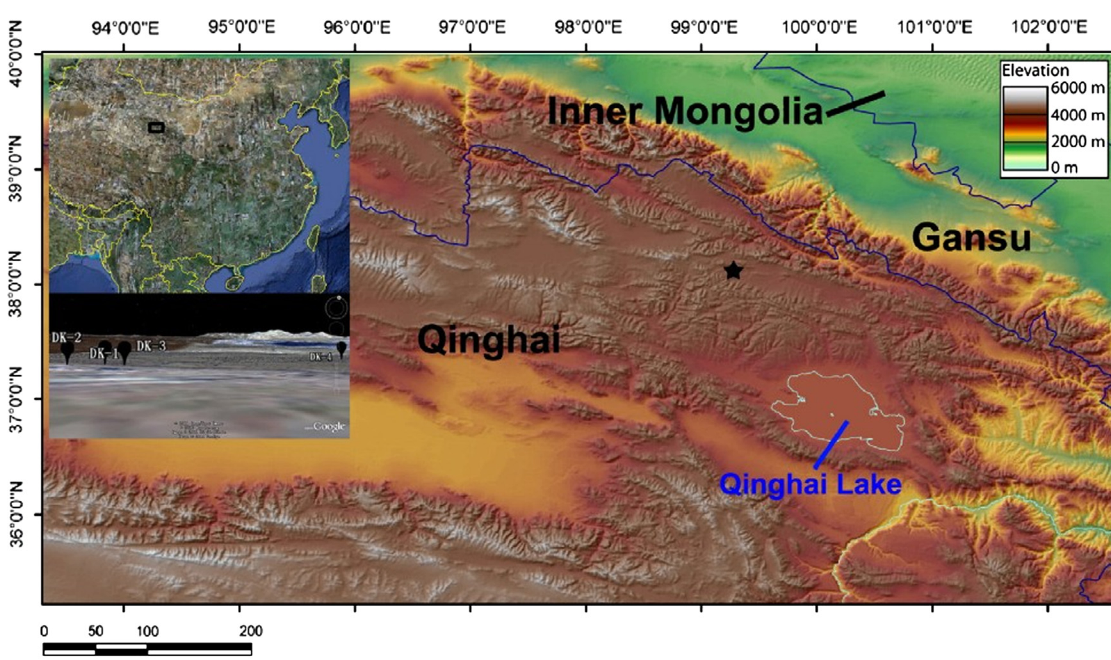


Fig. 2. Location and geomorphology of the study area. The black box and star indicate the study area and drilling area, respectively. The upper inset map presents a zoomed-out view of the study area. The lower inset map presents a zoomed-in view of the drilling area and shows the locations of the four drilling locations [28].

In 2005 and 2006, exploration research was conducted in the Shenhu area, and a drilling expedition ultimately began after feasibility analysis in 2007. To confirm the occurrence of gas hydrate, techniques including wire-line logging, sediment coring and sampling were utilized. Eight sites were investigated (Fig. 4) [33], with a pilot hole at each site. A sampling hole was drilled at sites SH1, SH2, SH3, SH5 and SH7, and gas hydrate bearing sediments samples were recovered at SH2, SH3 and SH7. Parameters including the sulfate-methane interaction, porewater salinity, chlorinity, and sulfate concentration were measured by wire-line logging [15]. According to the data, methane was the main component in all the samples, with 96.1–99.8% volume percentage in SH2, where the gas hydrate was determined to be the structure I type for the high C_1/C_2 ratio. The gas hydrate saturation was calculated from the pore water chemistry, resistivity and acoustic impedance [34]. Particularly for porewater freshening, the saturation was as high as 48% (v/v) at SH2, and the methane inventory in the research area was estimated to be approximately 2×10^9 m^3 at a 90% probability [15].

In September 2006, the South China Sea Institute of Oceanology of CAS conducted a “Northern SCS Open Cruise” to collect water column and surface water samples for methane concentration measurements. The sampling area is identified in Fig. 5 [35]. According to the measured data, the average value of the methane concentration was 3.8 ± 1.7 nmol/L, which is slightly higher than the values reported for other marginal seas and data based on atmospheric equilibria. Fig. 6 [35] illustrates the horizontal distribution of methane in the surface water of the northern SCS, indicating that the methane concentration gradients decrease with increasing distance from the shore. The methane concentration is mainly caused by input from the river and biological production, causing the concentration increase near the estuary. The vertical methane distribution of the water column along the continental shelf (transect B1–B10) is illustrated in Fig. 7 [35]. The methane concentration of the upper water is generally higher than that of the deeper water. However, an unusually high methane concentration (4.3 nmol/L) was measured at a water depth of 900 m, approximately 33 m above the sea floor at station B8 located southwest of the Dongsha Islands, which most likely originates from gas hydrates. The spatial distribution of methane in the northern SCS and the relatively high methane concentration provide evidence for the occurrence of gas hydrates in this area.

Afterwards, it was reported that samples of gas hydrates were successfully collected in the northern SCS during an exploration and drilling voyage conducted by the China Geological Survey (CGS) on May 1st 2007, confirming the enormous reserves of gas hydrates in the SCS. The samples were drilled at a depth of 183–201 m under the seabed, with a water depth of 1245 m. The thickness of the sediments containing hydrate was approximately 18 m, with a methane content as high as 99.7%. In June 2013, natural gas hydrate samples with high purity were drilled in eastern sea area of Pearl River Mouth Basin in SCS for the first time. The samples were drilled in two ledges at a depth of 220 m under the seabed, with a water depth of 600-1100 m. The average ore-bearing rate of natural gas hydrate in the cores is 45-55%, with the highest methane content as 99%. Through 23 drilling wells, the distribution area of natural gas hydrate is assessed to be 55 km^2,

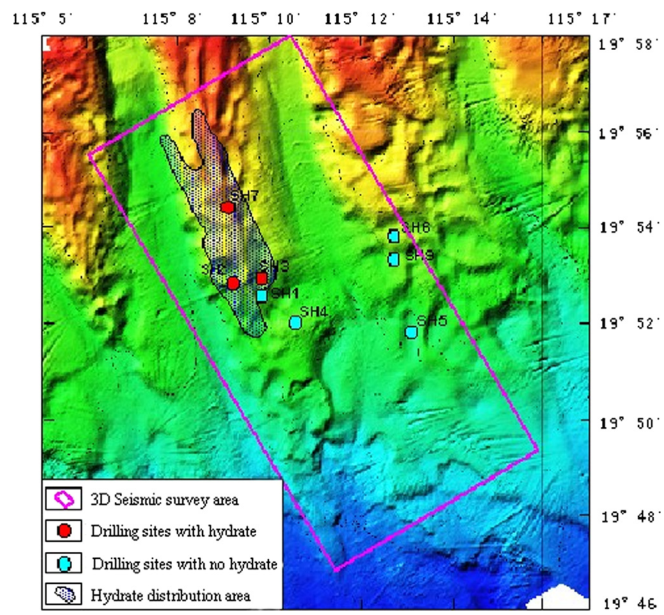


Fig. 4. Bathymetric map of gas hydrate drilling area and drilling sites in Shenhu area [33].

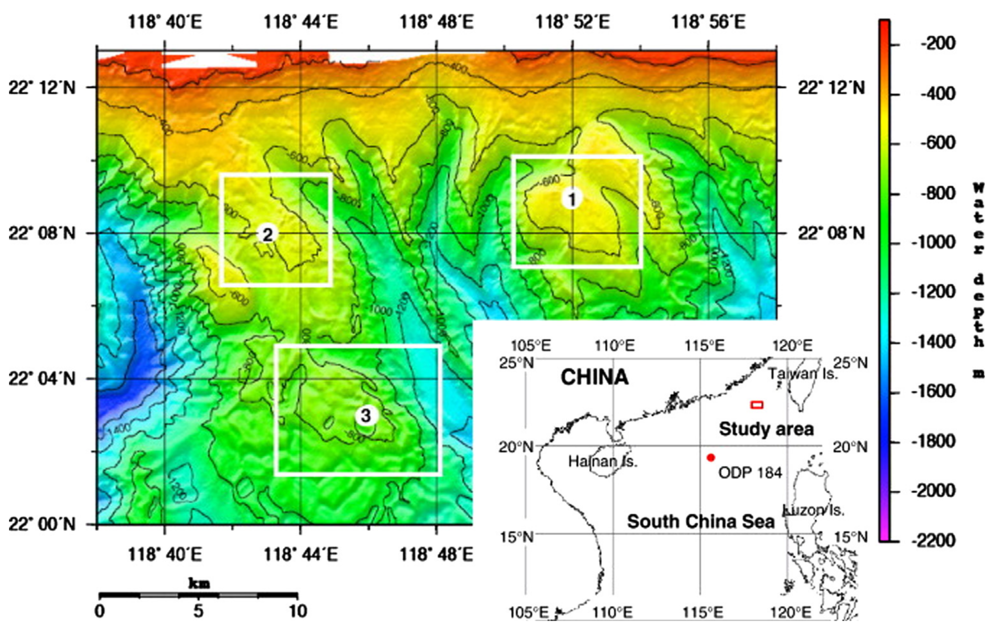


Fig. 3. Bathymetry of Jiulong methane reef in the northern SCS. Carbonates seep at sites 1, 2, and 3. Inset: Location of Jiulong methane reef [32].

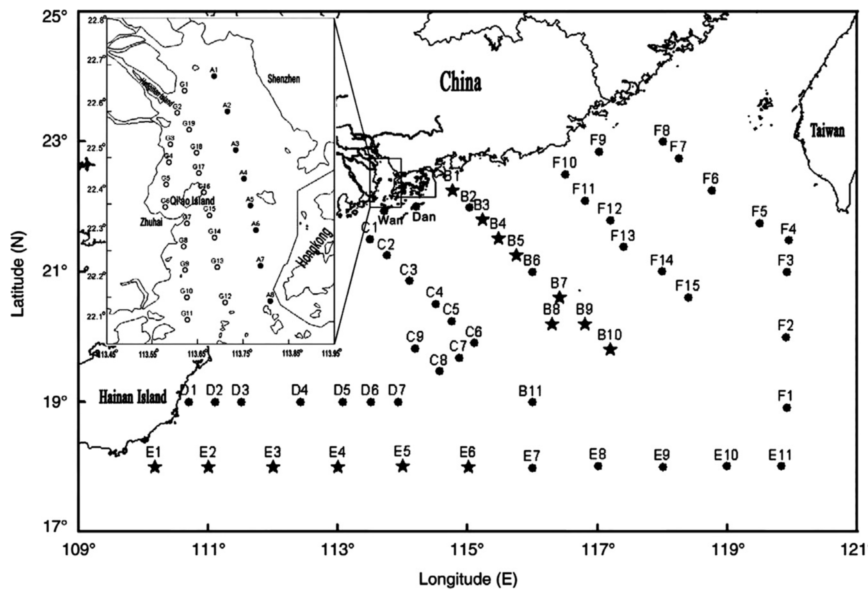


Fig. 5. Study area and sampling stations. Black stars: CTD stations; black circles: surface water stations [35].

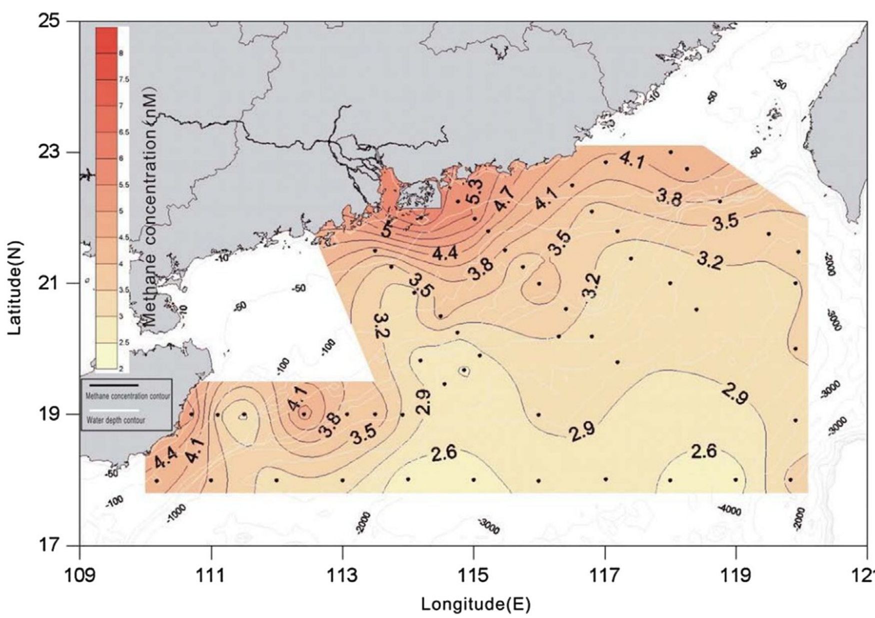


Fig. 6. Horizontal distribution of dissolved methane in the northern SCS [35].

and the controlled reserve of natural gas is approximately 100-150 billion m^3.

3. Basic gas hydrate property research in China

3.1. *Research on the fundamental phase equilibria of natural gas hydrates*

The phase equilibria of gas hydrates represent the most important set of hydrate properties, which determine the boundaries for kinetic problems such as formation and dissociation phenomena. Phase equilibria are also significant for exploring hydrate regions in marine sediment and permafrost areas and estimating the total reserves of gas hydrates. Many research activities have been conducted in China on the phase equilibria of gas hydrates and on the techniques based on hydrate phase behaviors.

Fig. 8 [36] shows the schematic of the experimental unit established in China University of Petroleum (CUP) for the gas hydrate phase equilibria investigation. Abundant phase equilibria data on gas hydrates formed by different gas components have been measured. According to Sun et al. [36], the hydrate formation conditions for methane and ethane gas mixtures in the presence of 0.06 mol fraction tetrahydrofuran (THF) in water were obtained at temperatures ranging from 277.7 to 288.2 K. These researchers observed that the hydrate formation pressure decreases with an increase in the ethane concentration in a pure water system, and the variation tendency of the hydrate formation pressure is the opposite with the presence of 0.06 mol fraction THF in aqueous solution. Moreover, the presence of THF in water can distinctly lower the hydrate formation pressure in most cases. However, when the ethane composition is as high as 0.82, it is more difficult to form hydrate in water with THF than without it, because it is easier for a methane molecule than an ethane molecule to occupy

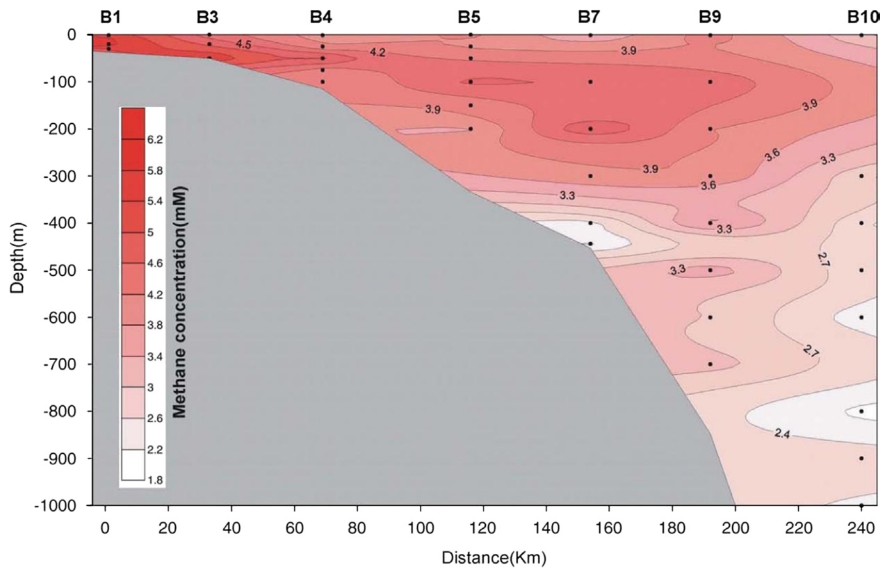


Fig. 7. Vertical distribution of dissolved methane ($nmolL^{-1}$) along the shelf in the northern SCS [35].

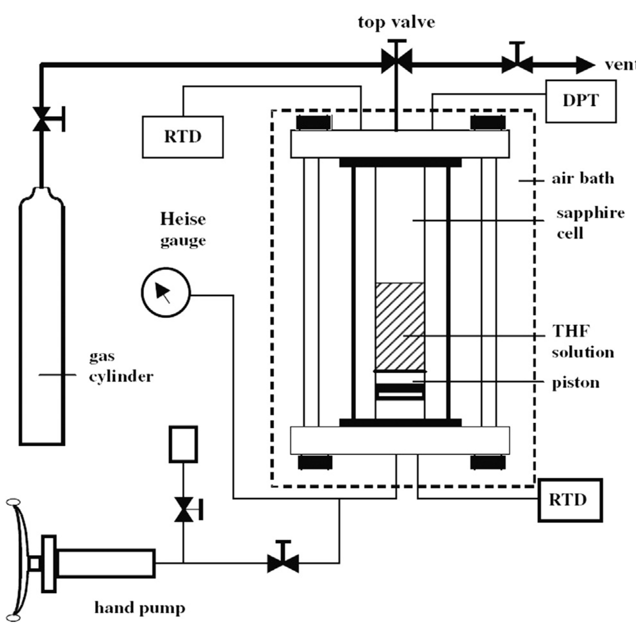


Fig. 8. Experimental apparatus for hydrate sample formation [36].

the smaller cavity of the hydrate structure at moderate pressure. Therefore, THF inhibits ethane hydrate formation while promoting methane hydrate formation. This result suggests a possible method to increase the efficiency of methane and ethane separation. In addition, Ma et al. [37] acquired hydrate equilibria data for systems containing hydrogen, methane, ethane and ethylene, both with and without THF in water and observed that hydrogen was efficiently separated from pure methane and gas mixtures of methane and nitrogen by forming a hydrate. In addition, the separation efficiency for hydrogen+methane gas mixtures in pure water and aqueous solutions with THF were examined under different temperature, pressure, and feed gas composition conditions by Sun et al. [38]. The results demonstrated that hydrogen was remarkably enriched in the vapor phase by a single equilibria stage with the existence of THF and that the H_2 purification effect increases slightly with an increase of the feed gas pressure. However, these hydrate equilibria data were almost all measured using the isothermal pressure and isobaric temperature searching methods. Both of these methods rely on a searching procedure by naked eye, which require a significant amount of time and cause measurement errors. The isochoric curve method, another method to measure hydrate phase equilibria data, is significantly more reliable and reproducible for porous media systems. Thus, Chen et al. [39] measured the equilibria conditions of gas hydrate in several systems using the step-heating method. Experimental hydrate phase equilibria data of CH_4/CO_2+sodium dodecyl sulfate (SDS) aqueous solution, CH_4/CO_2+SDS aqueous solution+silica sand, and ($CH_4+C_2H_6+C_3H_8$) gas mixture+SDS aqueous solution systems were obtained. Especially for a system consisting of silica sand, the equilibria pressure will change significantly when the particle size of the silica sand is less than 96 μm. Using the same method, Du et al. [40] measured the three-phase equilibria conditions of a ternary (hydrogen+*tert*-butylamine+water) system. The results indicated that the pure hydrogen hydrate phase equilibria pressure was reduced with the addition of *tert*-butylamine, meaning that *tert*-butylamine has effects similar to those caused by THF as a hydrate formation promoter. In addition, the concentration of the *tert*-butylamine solution has a significant effect on the three-phase equilibria curve ($H+L_w+V$). Furthermore, a significant amount of hydrate phase equilibria data for various hydrate formers was experimentally obtained by Fan et al. [41–45].

In addition to experimental studies, many researchers have made significant contributions to the simulation theory of hydrate phase equilibria. Song et al. [46] proposed an improved model based on the van der Waals and Platteeuw models of hydrate phase equilibria in bulk water and porous media by considering the interfacial energy in a hydrate-liquid–vapor system. The accuracy for predicting hydrate phase equilibria in a marine sediment environment can be improved using this suggested model. In addition, according to Li et al. [47], the hydrate equilibria dissociation conditions of single and mixed gases are predicted using two thermodynamic approaches, i.e., the fugacity model and the activity model, and good agreement between the calculated and experimental data has been obtained. For the simulation of gas mixture separation, an algorithm for a vapor-hydrate flash calculation was developed by Sun et al. [38] based on the extended Chen-Guo hydrate model, and good prediction precision was attained.

A pictorial summary of hydrate equilibria conditions in different systems is presented in Fig. 9. The variation tendencies of

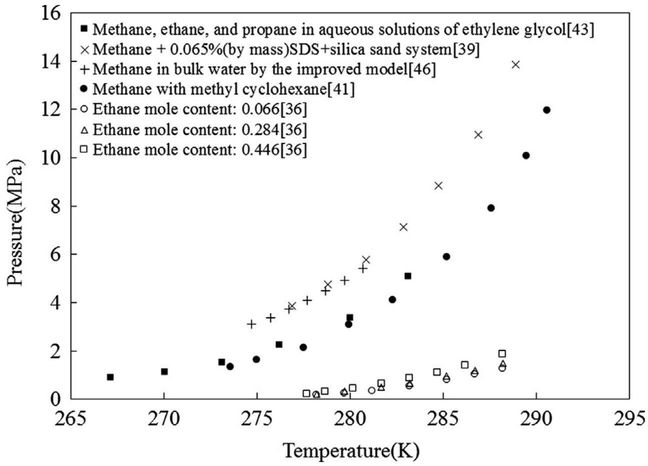


Fig. 9. Hydrate equilibrium conditions of different systems.

the phase equilibria curve with the mole content of ethane and methane phase equilibria in different formation environments are available. Detailed data can be found in the relevant Refs. [36,39,41,43,46].

3.2. Research on the formation mechanisms of natural gas hydrates in porous media

After understanding the phase equilibria conditions of natural gas hydrate formation, what we are most concerned about is how the gas hydrates form, grow and dissociate in porous media, especially on the micro scale. The dissociation and gas production processes of gas hydrates will be provided in detail in the following exploitation technology section.

Hydrate nucleation is the process during which water molecules framework as hosts attempt to trap gas guest molecules to achieve crystallization form. Guo et al. [48–50] has performed molecular dynamics simulations to study the formation mechanisms of gas hydrates. These researchers studied the evolution of cage-like water clusters immersed in bulk water and observed that the empty cage-like water clusters still have an opportunity to live long enough compared with cage-like water clusters filled with methane molecules, which support the cluster nucleation hypothesis [50]. In addition, whether the dodecahedral water cluster can naturally form in methane aqueous solutions was examined, which is a fundamental problem relevant to the methane hydrate nucleation mechanism [48]. An analysis method was developed to identify all face-saturated cages in a specific system, describing the amorphous phase during the spontaneous nucleation and growth of methane hydrate [49]. Additionally, Chen et al. [51] investigated the kinetic pathway of CO_2 hydrate formation using microsecond molecular dynamics simulations, and a three-stage process of CO_2 hydrate nucleation resulted.

The nucleation of water molecules with gas molecules can produce different structural forms of cages, known as s I, s II, or s H. The representative guest molecules of each structure are methane or carbon dioxide for s I, propane or THF for s II and cyclooctane for s H. Sun et al. [36] employed Raman spectroscopy to demonstrate the coexistence of structure I hydrate and structure II hydrate in the hydrate sample with THF in an initial aqueous solution. And with increasing THF concentration, only structure II was found, confirming the conclusions mentioned above that THF will act as an inhibitor to ethane hydrate with a specific amount. Studies have also been conducted on macroscopic phenomenon based on microcosmic hydrate structures, such as the memory effect, which can be succinctly described as gas hydrates retaining a type of memory of their structure when dissociating at moderate temperature. Consequently, gas hydrates will form more easily from gas and water obtained by dissociating hydrate than from fresh water. Wu et al. [52] conducted a series of experimental studies to investigate the effect of the memory effect on the nucleation of gas hydrate formation and its relation with the dissociation temperature. In addition, the memory effect between s I and s II gas hydrates was experimentally studied using reformation processes by Liu et al. [53]; the memory phenomenon was clearly observed in the alternate secondary formation of s I and s II gas hydrates. Furthermore, gas replacement, regarded as a new technique based on the hydrate structure, attracts the world's attention because of its effect of limiting the emission of CO_2 to the atmosphere and enhancing the recovery of natural gas from hydrates. Simulations were performed to study the mechanism of CO_2 replacement. The factors that affected the replacement rate were discussed based on the developed model, and the replacing procedure details were also determined by molecular dynamics simulation [54–56]. Gas production through CO_2 replacement will be discussed in detail in the following exploitation technology section.

The porous microstructure of natural gas hydrates governs the mechanical strength of the hydrate-bearing sediment and greatly affects the exploration of gas hydrate resources. In most cases, a natural gas hydrate forms in the pore space by floating, supporting, coating and cementation [57,58]. Zhao et al. [59,60] investigated the THF hydrate formation in a porous medium using magnetic resonance imaging. These researchers concluded that the dissolved quantity of THF in the water significantly affected how the THF hydrate grew, i.e., via the cementing mechanism at 19% concentration and via the floating mechanism as the THF concentration decreased. The observed behavior could have instructive significance in understanding seafloor stability and resource exploration if extended to methane hydrate.

3.3. Thermal physical properties of natural gas hydrates

Thermal data, representing the physical reality, form the basis for long-term theoretical developments. Therefore, studies on the thermal physical properties of gas hydrates are of significance not only for the future recovery of natural gas from hydrates, especially for the thermal stimulation method but also for the seafloor stability of gas hydrate-bearing sediments and plugging problem of natural gas transport pipelines.

Huang et al. [61] measured the thermal conductivity of methane hydrate formed from SDS solution using Gustafsson's transient plane source (TPS) technique. The values obtained were slightly smaller than the values reported in the literature for pure methane hydrates due to the gas pores with low thermal conductivity. To eliminate the effect of remaining gas in the pores, the cell was pressurized, and the thermal conductivity of the hydrate sample increased as a result. According to the experimental results, the thermal conductivity exhibits a well-defined positive temperature dependence, which is glasslike. Using a similar method, Li et al. [62] determined the effective thermal conductivity of methane hydrate in the dissociation self-preservation zone below the ice point, and an algorithm was established to predict the dissociation velocity of methane hydrate at different temperatures based on the measured thermal conductivity. The data revealed that the thermal conductivity increased with an increase in temperature due to the increase of the ice fraction, with larger thermal conductivity occurring during dissociation. In addition, the calculated dissociation velocity was very low in the temperature range from 263.15 to 271.15 K because of self-preservation, during which 268.15 K was associated with the lowest dissociation velocity of methane hydrate. At 1 atm and 268.15 K, the total gas that evolved after 24 h accounted for less than 0.71% of the initial stored gas,

which can be considered as ultra-stability and the best temperature point to store methane hydrate. In addition, a study on heat transfer and utilization during hydrate dissociation will provide an effective theoretical basis for future large-scale hydrate exploitation. Li et al. [63] investigated methane hydrate production during three-dimensional thermal huff and puff, and the thermal efficiency and energy efficiency were employed to evaluate the gas production efficiency from the gas hydrate reservoir. According to their work, there are high thermal efficiencies and energy efficiencies in the first 4–5 cycles, which are the optimum period for gas production using this method. However, the effect of increasing the injection temperature and injection time is not apparent in enhancing the economic effectiveness during hydrate dissociation, and the highest thermal efficiency and energy efficiency can be obtained with an injection temperature of 130 °C and an injection time of 5 min. These researchers also observed that the injected heat does not diffuse isotropically in the hydrate reservoir. A methane hydrate dissociation experiment using a thermal method was also conducted by Pang et al. [64], and the rate of heat transfer and the thermodynamic driving force were observed to be the key rate-determining factors of the hydrate dissociation. In addition, Zhao et al. [65] conducted a heat transfer analysis of a methane hydrate sediment during dissociation in a closed reactor using a thermal method; thermal conductivity measurements during the gas hydrate dissociation are being performed, and the effect of heat transfer on gas hydrate dissociation is being evaluated. Furthermore, an investigation on the relationship between the effective thermal conductivity and the physical properties of the sediments will soon be conducted using X-ray CT to determine the pore structure and the medium content.

Fig. 10 presents the thermal conductivities and composite thermal conductivities of hydrates in sediments measured by Huang et al. [61,66]. The relationship between the thermal conductivity and temperature and the effects of phase saturation and sediment type are illustrated.

3.4. Research on the acoustics and resistivity characteristics of natural gas hydrates

Characterization of natural gas hydrate occurrence in sediments is of importance in hydrate exploration and gas production from gas hydrate reservoirs. The formation of gas hydrates in the voids of deposits can significantly change the fundamental

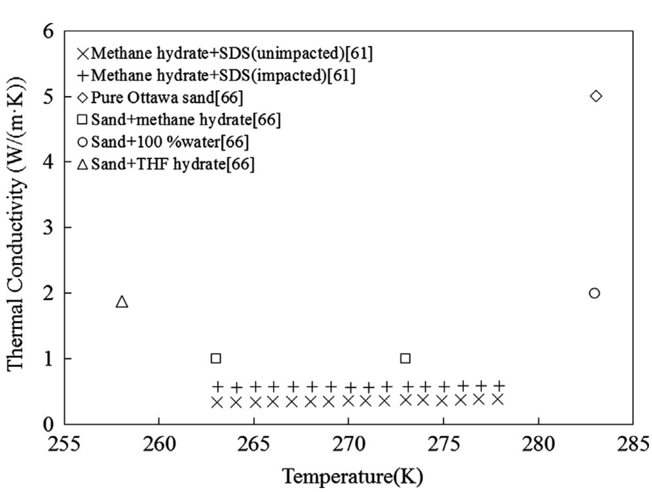


Fig. 10. Experimental data of hydrate thermal conductivity and composite thermal conductivity.

features of the matrix, including the acoustics and resistivity characteristics. Research on the acoustics and resistivity characteristics of natural gas hydrates can be employed in determining hydrate saturation, distribution and other properties of gas hydrate-bearing sediments.

Ren et al. [67] has conducted experiments to measure the acoustic P-wave velocity of sandpacks with methane hydrate formed under simulated subsea sediment conditions. Ultrasonic waveforms are formed during the process of hydrate formation, indicating that the acoustic velocity and amplitude of the acoustic waves increase with hydrate formation. This finding can be explained because the gas hydrate formation in the sediment could consolidate the matrix, enhancing the cementation between sand grains. In addition, the variation tendency of the sound velocity with hydrate saturation is well modeled by a revised Wyllie Equation in this study. The gas hydrate saturation in the Shenhu area in the South China Sea was determined by Wang et al. [34] from acoustic impedance, which was calculated from 3D seismic data using the constrained sparse inversion method. The results illustrate that the estimated gas hydrate saturation was 10–23% of the pore space, which is comparable to the results estimated from the well logs. Hu et al. [68] also experimentally investigated the acoustic properties of gas hydrates during hydrate formation and dissociation processes in unconsolidated sediment using ultrasonic detection and time domain reflectometry (TDR) techniques. The experimental data revealed that gas hydrate forms in the pore space to cement the sand grains at hydrate saturation of 0–1%, resulting in a sharp increase in the compression velocity and wave attenuation. In addition, similar studies were conducted on the ultrasonic detection of gas hydrate formed in artificial cores, and the relationship between the well-logging acoustic wave velocity and hydrate saturation were also determined [69–71].

In addition to acoustic characteristics, resistivity also represents a basic physical property of a gas hydrate that can be acquired from well logging. Wang et al. [34,72] conducted relevant research to determine the gas hydrate saturation from resistivity data based on the standard and modified Archie equation. The results demonstrated that the gas hydrate saturation estimated from isotropic resistivity of site SH2 in the Shenhu area had an average value of 24% with a maximum value of 44%, which coincides well with the values estimated from chloride anomalies. Furthermore, resistivity measurements of gas hydrates during the formation and decomposition processes in a porous medium were performed by Li et al. [73,74]. According to the results, the resistivity of the sample declined to a minimum value of 2–3 Ω m when the gas hydrate began to nucleate and then increased to a great extent as the gas hydrate grew, with a final value of 11–13 Ω m representing the completion of the formation process. Therefore, the resistivity measurement verified the feasibility of monitoring the nucleation and growth processes of a gas hydrate. In addition, analogous conclusions were drawn by Ren et al. [67] and Zhou et al. [75] that the resistivity of the sandpack bearing hydrate would slightly decrease when the hydrate saturation was low ($<20\%$) and increase at higher hydrate saturation ($>20\%$).

4. Exploitation technology investigation in China

Because natural gas hydrate has attracted the world's attention as a type of potential energy, developing feasible methods for commercial production of natural gas from hydrate reservoirs is essential. To date, three common methods for gas production have been proposed: depressurization, thermal stimulation, and inhibitor injection [76]. In this section, recent progress in research on

the exploitation technology of natural gas hydrates in China is briefly discussed, mainly focusing on the first two methods.

4.1. Depressurization method

Yang et al. [77] performed a hydrate dissociation experiment using depressurization at a constant pressure of 1.0 MPa using a middle-scale reactor equipped with 16 thermocouples to investigate the gas hydrate dissociation behavior in three dimensions. The temperature field and gas production were primarily studied. The researchers observed that no obvious decomposition front exists in the hydrate bearing sediments, as the temperatures decrease sharply in all locations during the initial stage of dissociation. However, the hydrate decomposition rates at different locations are not uniform, with those at the sample center being lower and controlled by the heat transfer. The gas production rate, which is mainly affected by thermal buffering and heat transfer as well as the ice layer arising from hydrate dissociation, is faster during the beginning stage. Therefore, conclusions are drawn that it may be more reasonable for the depressurization method to be used during the initial stage of the gas production followed by other methods for further recovery of natural gas. To reveal the dependence of the production behavior on the size of the hydrate reservoir, Li et al. [78–82] compared the experimental results of gas production behavior from methane hydrate by depressurization in a novel pilot-scale hydrate simulator (PHS) with an effective volume of 117.8 L with that in a cubic hydrate simulator (CHS) with an effective volume of 5.8 L. Abundant experimental data were obtained, and many parameters including cumulative gas production, pressure change, water production, temperature spatial distributions were discussed in detail. The results indicated that the progress of gas production in the two simulators could be divided into three periods: the free gas production, mixed gas (free gas and gas dissociated from the hydrate) production and gas production from hydrate dissociation. The cumulative gas production in the third period with each of the PHS and CHS was much larger than those in the first or second period but with a lower gas production rate. Particularly because of the low production rate, the production time from 60% to 100% of the dissociated gas production took up approximately 70% of the entire dissociated gas production time; therefore, other methods should be used to enhance the gas recovery efficiency as proposed above. In addition, the duration time for the dissociated gas production period of PHS was approximately 20 times that of CHS, illustrating the significant dependence of the production behavior on the size of the hydrate reservoir. For water production, the CHS reached a relatively high rate in the first two periods, while a low rate was observed for the entire gas production process with the PHS. Moreover, the temperature change tendency of the CHS was almost the same as that of the PHS except for a temperature increase resulting from the hydrate reformation. In addition, Su et al. [83] examined the decomposition behavior of methane hydrate in 20–40 mesh natural sand with a salinity of 3.35 wt% using a 3D experimental device with an inner diameter of 300 mm and an effective height of 100 mm, and the temperature curves indicated that the hydrate at the top and bottom of the reactor dissociated earlier than in the middle.

The production potential of the laminar hydrate deposit at drilling site SH3 in the Shenhu area was evaluated using numerical simulation through depressurization using vertical wells [84,85]. The simulated results indicated that gas production by depressurization at constant well pressure through a vertical well does not function well in the deposits of low hydraulic diffusion with an average production of 211 m^3/d. In addition, the most insensitive parameter to enhance gas production was the deposit permeability.

4.2. Thermal stimulation method

Another method to exploit natural gas hydrate reservoirs is thermal stimulation, in which the hydrate deposits are heated above phase equilibria temperature by in situ combustion or a hot water steam injection. Li et al. [63,86–88] investigated the decomposition behaviors and gas production of methane hydrate in porous media using the huff and puff method in two simulators with different scales, which were mentioned previously. The results from the CHS indicated that the rate of gas production decreased with an increase of cycle number, and an increase of the injection temperature and injection time could enhance the cumulative gas production. The average gas production rate during the entire huff and puff process was approximately 0.21 L/min. The experimental date from the PHS indicated that with a constant injection rate, the thermal diffusion was restricted around the well, resulting in the gas production being dominated by depressurization rather than thermal stimulation, while prolonging the hot water injection time could improve the gas production efficiency. Compared with the CHS, the average gas production rate of the PHS was much higher, at 2.87 L/min. Additionally, the kinetic behaviors of methane hydrate dissociation in a reactor of 10-L volume were studied by Pang et al. [64] using the hot water stimulation method. A dissociation buffering phenomenon resulting from melting ice was observed, causing a significant decrease in the hydrate dissociation rate. Increasing the heating fluid temperature and decreasing the dissociation pressure was observed to reduce the buffering effect. Conclusions were also drawn that the optimized method to increase the hydrate dissociation rate during gas production was to combine the depressurization and thermal stimulation method. Furthermore, Li et al. [89] employed microwave (MW) heating instead of the traditional stimulating method and observed that the hydrate dissociated more rapidly than when using the hot water heating method under the same heating power. The hydrate dissociation rate appeared to be a function of the microwave power with a proportionality relationship, and the temperature increased linearly with time during microwave radiation.

In addition to experimental research, relevant numerical simulations of gas production potential from specific natural gas hydrate reservoirs have also been performed. Su et al. [90] simulated the hydrate dissociation and gas production by alternately injecting hot water and producing fluids from gas hydrate deposits in the Shenhu area of the South China Sea through a vertical well. The calculated gas production rate was very low at 50–140 m^3/d, which is unacceptable for commercial production. In addition, the gas production potential from hydrates at the DK-3 drilling site of the Qilian Mountain permafrost located in the north of the Qinghai–Tibet plateau was numerically investigated by Li et al. [91,92].

4.3. Other methods

In addition to the two methods mentioned above, other methods including the depressurization and thermal stimulation combination method and CO_2 replacement method are also alternative methods of gas production. To investigate the propitiousness of the depressurization and thermal stimulation combination method for gas production from gas hydrate, Li et al. [93] performed an experimental study using a specially designed experimental system. The gas hydrate dissociation experiment was performed by injecting hot-brine and then decreasing the pressure, and the changes in temperature, resistivity, gas production rate and energy efficiency during dissociation were analyzed. The results indicated that the combination method could achieve higher energy efficiency and appears to be an optimized method of

gas production. Liu et al. [94] also experimentally evaluated the combination method, and higher production efficiency and shorter dissociation duration times were reported. Moreover, Bai et al. [95] simulated gas production from a hydrate reservoir using the combination of warm water flooding and depressurization. In their work, physical and mathematical models were developed to simulate the hydrate dissociation. And the numerical results demonstrated that the combination method could obtain a longer stable period of high gas rate than the single production method under certain conditions. In addition, numerical studies of gas production from a gas hydrate zone in the Shenhu area using the combination method were conducted by Hu et al. [96]. The calculated results verified the advantages of the combination method over the single method on gas production efficiency and demonstrated that the temperature was not sensitive to the CH_4 production rate.

Additionally, Zhao et al. [97] reviewed studies on the replacement of CH_4 in natural gas hydrates using CO_2, and the feasibility of the replacement was proven, the latest progress in CH_4 replacement experiments with CO_2 in different phase states was presented, and the optimum conditions for the replacement with different forms of CO_2 was suggested. The favorable conditions for methane recovery from gas hydrate using gaseous carbon dioxide were experimentally investigated by Yuan et al. [54], and the replacement mechanism was assumed to include two parts: CH_4 hydrate dissociation and mixed hydrate re-formation. A kinetics model was constructed to describe the replacement process, and the calculated results agreed well with the experimental data. In addition, according to the simulation, the initial CO_2 mole fraction, a decrease in the system pressure, and an increase in the diffusion coefficient of CH_4 in the hydrate layer were proven to be sensitive factors of the replacement rate. After analyzing the equilibria relations of CH_4 and CO_2 hydrates as well as the geotherm and gaseous–liquid curve, Zhou et al. [98] divided the replacement area into 5 parts, and relevant replacing experiments were conducted. The results revealed that the replacement rate with CO_2 emulsion was much greater than other phase states due to the excellent conductivity and diffusibility of the emulsion, which provided an effective support for future exploitation. In addition, the replacement of methane from hydrate in porous medium using a carbon dioxide-in-water emulsion and high-pressure liquid CO_2 was performed by Zhou et al. [99]. In addition, it has been demonstrated experimentally that a CO_2 emulsion has advantages when replacing CH_4 from a hydrate compared with high-pressure liquid CO_2. Moreover, a molecular dynamics simulation performed by Qi et al. [55] also resulted in a similar conclusion that it is difficult for a CO_2 molecule to penetrate into the interior cages of the CH_4 hydrate via dissociation. This finding means the replacement process most likely includes a cage-breaking step.

In addition, Fan et al. [100] has performed hydrate dissociation experiments using the addition of ethylene glycol as an inhibitor, and the concentration and flow rate of the ethylene glycol were proved to be important factors in determining the dissociation rate.

5. Security of nature gas hydrate exploitation

Large quantities of CH_4 are stored in marine sediments in the form of methane hydrate, which is considered a potential future energy resource with characteristics of high energy density, significant amounts of resources and cleaning. Determining how to acquire natural gas from the hydrate as a possible energy supply is becoming a focused issue. However, the security of natural gas hydrate-bearing sediments during exploitation and the effect on the atmosphere must be considered.

5.1. Mechanical properties of natural gas hydrate-bearing sediments

Currently, the feasible way to acquire natural gas from a hydrate is to first decompose the hydrate into sediments and then to collect the gas and transport it to the surface of the ocean or permafrost. However, the dissociation of methane hydrate during exploration and exploitation may result in seabed subsidence and hydrate sediment stratum deformation. Considering the exploitation security and the hydrate reservoir stability, studies on methane hydrate mechanical properties are of great importance.

In China, few research groups are focusing on the mechanical behavior of methane hydrate, among which Dalian University of Technology (DUT) is making great efforts on this field. Table 2 [101–105] presents a comparison of the parameters of triaxial testing systems of three institutions in China. A schematic diagram of the triaxial testing system at DUT is presented in Fig. 11 [106]. Using this testing system, abundant experimental data on the mechanical properties of methane hydrate were obtained [101,102,106–110]. Song et al. [101,102,107–110] conducted a

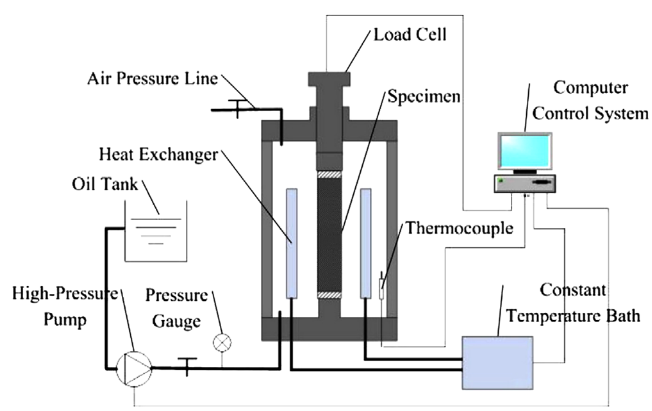


Fig. 11. Schematic diagram of triaxial testing system [106].

Table 2
Comparison of triaxial testing system parameters established in China [101–105].

	CAS	CUP	DUT1	DUT2
Maximum axial load/kN	100	100	60	600
Maximum pressure in pressure chamber/MPa	14	30	30	30
Maximum backpressure/MPa	10	20	20	20
Sample size/mm	Φ39.1 × 80	Φ25 × 50, Φ50 × 100	Φ50 × 100	Φ150 × 300
Temperature range in pressure chamber/°C	−20–20	−25～Normal temp Accuracy:0.5	−20～Normal temp Accuracy:0.5	−20～Normal temp Accuracy:0.5
In-situ formation	/	/	/	Yes
Dynamic load	/	/	/	Yes
Permeability and dissociation rate measurement	/	/	/	Yes

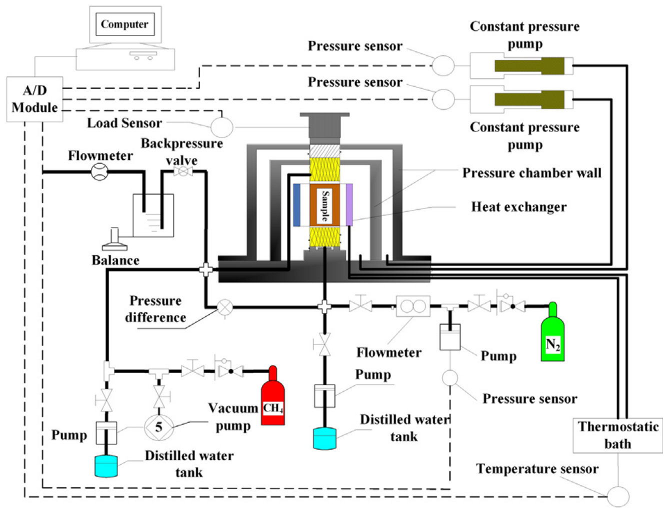


Fig. 12. Schematic diagram of the new triaxial testing system established in DUT.

series of triaxial shear tests under various conditions to study the mechanical characteristics of artificial methane hydrate–ice mixture specimens. The effects of confining pressure, temperature, strain rate and hydrate content were discussed. The preliminary results indicated that an increase in the confining pressure enhanced the shear strength when the confining pressure was less than 10 MPa. In addition, the shear strength increased with a decrease of temperature and methane hydrate content and increasing strain rate. A modified Mohr–Coulomb criterion considering the effect of methane hydrate content on shear strength was proposed [101]. Based on the test data, axial strain-dependence curves were obtained, which can be divided into two stages: the rapid structural damage stage and the complete structural damage stage. In addition, a modified nonlinear elastic Duncan–Chang constitutive model was proposed to clarify the stress–strain behavior of artificial methane hydrate–ice mixtures [106]. Furthermore, Song et al. [108–110] studied the mechanical properties of methane hydrate-bearing sediments that were formed using kaolin clay. The effects of temperature, confining pressure, strain rate and porosity on the shear strength and deformation behavior were clarified. A strength criterion considering the effect of temperature was established, and the Duncan–Chang model was improved to establish the constitutive relation model for methane hydrate-bearing sediments [108,110]. Recently, to investigate the mechanical characteristics of real seafloor sediments, a new triaxial testing system has been developed at DUT (Fig. 12) under the support of the CNOOC Research Center. This system was modified to simulate seafloor sediments by forming natural gas hydrate in-situ in the sample pressure chamber, and dynamic load, permeability and dissociation rate measurements are performed.

Researchers from other scientific establishments in China have also significantly contributed to investigation of the mechanical properties of methane hydrate. Zhang et al. [111] from China University of Mining & Technology (CUMT) reviewed the advances in research on the mechanical properties of gas hydrate from experimental and numerical aspects. Some theories on strength and deformation were introduced, and a simple constitutive model for gas hydrate-bearing sediments was developed. Lu et al. [103,105] from CAS performed a series of experiments to study the mechanical properties of tetrahydrofuran hydrate and methane-hydrate-bearing sediments. The stress–strain curves and strength parameters of pure tetrahydrofuran hydrate and methane-hydrate-bearing sediments were obtained and discussed. Moreover, Sun et al. [104] from CUP and Zhang et al. [112] from QIMG performed relevant investigations related to the mechanical behavior of methane hydrate.

5.2. Environmental aspects of gas hydrates

Today, the large impact of greenhouse gases (GHGs) on the climate and environment, known as global warming, has been realized worldwide. Methane, as a type of GHG whose global warming potential index (GWP) is 3.7 times that of CO_2 by mole number and 20 times by weight [113], contributes much more than carbon dioxide to the greenhouse effect. The release of large volumes of methane from hydrates into the ocean and atmosphere could have significant effects on marine ecosystems and the climate. Researchers have observed that an ancient massive marine methane hydrate dissociation caused a 4–8 °C temperature rise over a geologic period called the Late Paleocene Thermal Maximum (LPTM) that occurred 55.5 million years ago [114].

In addition to the atmospheric environmental effect, the escape of methane from marine gas hydrates could also induce marine ecosystem disasters, which would eventually affect the biological species balance on the Earth. Based on the records of core high-resolution carbon isotopes from site 892 in the Ocean Drilling Program (ODP Leg146) and site 995 (ODP Leg164), scientists believe that large quantities of methane being released from gas hydrates in a short period was the direct reason why 1/2 to 2/3 of benthic animals became extinct at the turn of the Paleocene and Eocene [2].

Considering the possible hazards to the atmospheric and marine environment and the relatively low level exploiting technique, the large-scale development and utilization of these resources are still tentative. With the improvement of technology and the accumulation of exploiting experience, it is likely that one day, mankind will need to become involved in the ocean to meet growing energy demands.

6. Conclusions and prospects

In this paper, the latest research activities performed by Chinese researchers are briefly reviewed, including an exploration of natural gas hydrates in permafrost areas and the continental slope, basic property research (i.e., determination of phase equilibria, structural properties, thermal physical properties and acoustics and resistivity characteristics), exploitation techniques and the security of hydrate exploitation. This work represents the major work that has been recently performed in China but is not complete.

Gas hydrates are a vast resource, the reserves of which are sufficiently enormous that they deserve evaluation as a potential and sustainable energy source. Considering the worldwide energy crisis, gas hydrates have attracted international awareness. Currently in China, significant challenges need to be overcome in the commercial exploitation of natural gas hydrate resources; therefore, numerical simulation theories and experiment research on gas hydrate mining technology in the laboratory seem particularly significant in providing fundamental data and operating conditions for test mine fields. Meanwhile, safe and efficient exploitation of gas hydrate requires fully integrated and comprehensive assessment of the environment impact and positive countermeasures of environmental protection. The development of a clean and efficient gas hydrate applied technology is the decisive factor for the commercialization of natural gas hydrate resources. Although the research level in China is still in its early developing stage, with research groups and governmental agencies increasingly becoming involved in this field, and with additional financial and political support, there is no doubt that the research quality

and scientific contribution will reach a new stage, and we are convinced that gas hydrate will eventually benefit mankind in the near future with constant effort and diligence.

Acknowledgments

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